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May- August 1928) on pages 195 to 197, July 1928. By  
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### "Herapathite"

The purpose of the task described in the foregoing article was to make a sol or at least a comparatively stable suspension of any substance with very pronounced optical properties which also is known in the form of well formed, rod - shaped or tablet - shaped crystals. Such a system would have the theoretical advantage that any optical properties of the same could be attributed to the known crystals whereas in the case of the known sols, with double refraction of the flux for example, conclusions could only be drawn on the contrary from the behavior of the sol as a whole on the properties of the disperse phase and some uncertainty attaches to this.

Of a substance adapted to the purpose described it must be required a priori that it crystallizes from a number of solvents well in individual crystals and is neither dissolved nor decomposed by a considerable number of fluids.

The known requirements appear to be fully met by herapathite ( iodoquinine sulfate) and accordingly a lengthy series of tests for the purpose of bringing the same into a state of sufficiently fine dispersion were instituted. This optically highly remarkable substance is always mentioned in manuals on the subject(1) and serves also for the micro-chemical detection of quinine(2) but otherwise it appears to be

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but little known so that what is important is reproduced here from the not very extensive literature.

Influenced by a chance remark of one of his pupils W. B. Herapath obtained this substance by precipitation from a hot solution of quinine bisulfate in acetic acid with alcoholic iodine solution. He described this very explicitly in two articles (3), the first of them under the title "Concerning the optical properties of a recently discovered quinine salt which crystalline substance has the ability to polarize light like tourmaline etc." which contains important material for our purpose.

On the cooling of the reaction mixture the compound separates out in splendid, metallic, glistening crystals of small size which Herapath compares to the "wings of the Spanish fly". They are either long, rectangular or hexagonally rounded, very thin tablets. Striking is the strong polarization or, speaking more exactly, the extremely high absorption of the one beam formed in the double refraction in consequence of which even very thin crystals let through purely rectilinearly polarized light. This is very distinct in the microscopic image owing to the fact that the point of intersection of two crystals crossed at right angles which are regarded in ordinary light is black as midnight (Herapath) even if the same are only 0.05 mm. thick. Fig. 1 is a microphotograph taken with ordinary light of a group of typical crystals with numerous points of intersect-

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ion. The highly pronounced dichroism ( almost colorless-black- violet) is to be seen in fig. 2 which shows the same crystal group illumined with rectilinearly polarized parallel light.

The crystals keep for an almost unlimited time under concentrated acetic acid; likewise when they are filtered off, washed with acetic acid and then with alcohol and dried at room temperature. In boiling alcohol they dissolve to form a clear reddish- brown and crystallize out again when cooling but, as Herapath observed, no longer in individual crystals but always in rosettes or stars. On contact with water they lose almost instantly the greenish, metallic gloss and are decomposed.

For this reason only organic dispersion agents are to be considered. The usual methods were ~~nexted~~ tried, namely: 1. carrying out the formation reaction in great dilution and 2. pouring the solution( hot) into a considerable number of dispersion agents. None of the methods led to the desired goal although perhaps this failure may be of interest in view of the unusual nature of the problem.

1. If we carry out the reaction of Herapath with a very low quinine concentration the solution will remain completely clear and no formation of precipitate will occur. If we use higher concentrations but add to the estimated amount of iodine

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only four to five drops of iodine solution to about 50 ccm. of a ten percent quinine bisulfate solution in glacial acetic acid, then the mixture on cooling will remain supersaturated for a comparatively long time but finally macroscopic crystals will be separated.

2. As dispersion agents were investigated: glycerin, ethane tetrachloride, methane tetrachloride and benzyl alcohol. Either the reaction mixture or a hot solution of the crystallized substance in methyl or ethyl alcohol was poured into an excess of the dispersion agent. In glycerin and the chlorinated hydrocarbons the substance necessarily gave up some iodine; if, as was the case with the latter on account of the limited miscibility with acetic acid the hot alcoholic solutions were used then the substance finally crystallized out as it would from alcohol alone in macroscopic aggregates.

Then the attempt was made to retard the crystallizing out by addition of a protective colloid. As such there are to be considered in acetic acid only cellulose nitrate and - acetate, the latter in benzyl alcohol too. In this dispersion agent cellulose acetate behaves in a manner similar to gelatine in water; it swells in the cold, is dissolved at 40° and forms a sol which on cooling and with sufficient concentration forms an elastic jelly.

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The nitrate proved to be unusable as decomposition takes place with separation of iodine. Herapathite dissolves in hot benzyl alcohol very well to form a reddish- brown solution; if this was poured into a great excess of acetate benzyl sol the mixture remained for a long time supersaturated but finally the substance separated in macroscopic, black, glistening spheres covered with spikes and spheroliths. This occurred even with an acetate concentration of 2.5 percent in the case of which on cooling to room temperature a noticeable jelly formation took place.

As these variants of the usual methods have been ~~more~~ proven to be unserviceable the attempt was made to carry out the reaction in such a way that the substance separates at once with sufficiently high degree of dispersion , that is, with extremely high degree of concentration. The reaction proceeds even in the cold ( that is the way it is conducted in the case of microchemical detection) and in the event of very slight solubility of the substance in cold acetic acid it seemed indicated to choose this way. After some orienting tests the following process seemed to be successful.

We introduce into a small porcelain dish 4 g. of a finely pulverized quinine sulfate ( not bisulfate) pour a mixture of 5 ccm. 20 percent iodine solution into alcohol and 3 ccm. glacial acetic acid and stir with a glass rod continuously in a vigorous manner. The dark- brown color of iodine soon

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disappears and the mixture becomes colored gray-black; we continue the stirring until the characteristic bronze - green surface shimmer shows which, however, owing to the very slight average size of the herapathite crystals is not evidenced very intensively, even being imperceptible. The mixture which contains free quinine sulfate can be kept for days without a noticeable diminution in dispersion occurring.

Further we suitably prepare one or two days before a sol by dissolving 1. 5 g. cellulose acetate in 100 g. glacial acetic acid and filter, if necessary, through a glass wool filter. If into this amount of sol we introduce four to five small drops of the above described reaction mixture and mix by vigorous shaking then we shall obtain a comparatively stable suspension with right striking optical properties.

In considerable thickness it becomes quite opaque, in incident light it is gray with slight metallic luster; if *it* the fluid is moved then we see glossy metallic streaks. In a thickness of 7- 8 mm. the suspension is brown in ordinary light and quite turbid; on being stirred, light, almost colorless and comparatively transparent streaks appear. The streaks disappear owing to the comparatively high viscosity of the dispersion medium but slowly so that a bright portion may be regarded with the Nichols prism. This will appear light if the plane of oscillation is vertical to the longitudinal direction of the light streak and dark if it stands parallel to it.

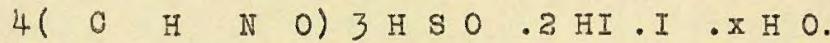
These right striking phenomena can be immediately explained by the optical properties of the herapathite crystals. If we regard the microscopic image in ordinary light (fig.1) then it is clear that a greater number of irregularly arranged crystals must cause at the points of intersection through extinction a considerable weakening of the incident light. At places where the crystals are placed parallel no extinction takes place on the contrary and these places accordingly appear light when one looks through them.

Likewise we can explain the appearance of a light streak when observing with a Nichols prism as due to dichroism (fig.2). The crystals directed parallel with the longitudinal axis of the plane of oscillation of the ~~xxxstazt~~ Nichols prism appear dark, those vertical thereto light and almost colorless. The crystals in the light streak lie in such a way that their long axes are approximately parallel.

The suspensions are deposited within about 48 hours but the flocculation apparently is quite reversible and after vigorous shaking the system shows the same optical properties as previously. However we are only speaking here of the above described phenomena which are easy to observe; a more thorough investigation I have not carried out owing to insufficient apparatus. However I have asked of Prof. H. Freundlich whether he could help me with the means at his disposal and am glad to report that he has declared his readiness to do so.

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In conclusion it may be of interest to mention that herapathite (and other azid periodides of quinine and related bases) have been very thoroughly investigated by S. M. Jorgensen (4) who gives it the formula



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see original for foot- notes

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→ set forth as  $4(\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2) \cdot 3\text{H}_2\text{SO}_4 \cdot 2\text{HI} \cdot 4\text{H}_2\text{O}$   
in net 1.457 664 lb/d  $\times 65 - 65$